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# (54) Procedure for the production of alkyl carbonates

Verfahren zur Herstellung von Alkylcarbonaten

Procédé pour la fabrication de carbonates d'alkyle

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(56) References cited:
EP-A- 0 354 970
EP-A- 0 366 177
EP-A- 0 445 891
EP-A- 0 460 732
DE-A- 3 016 187



EP 0 534 545 B1

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## Description

The present invention relates to a procedure for the production of alkyl carbonates.

More specifically the present invention relates to a procedure for the production of alkyl carbonates, and in particular dimethyl carbonate, starting from carbon monoxide, oxygen and an alcohol in the presence of a cuprous halide as catalyst.

Alkyl carbonates are extremely versatile products which are used as organic solvents and as additives for fuels, or as reagents, as a substitute of phosgene, in the synthesis of other useful alkyl or aryl carbonates such as synthetic lubricants, solvents, plasticizers and monomers for organic glass and in methylation and carbonylation reactions for the preparation of isocyanates, urethanes and polycarbonates.

The usual method for preparing alkyl carbonates consists in the reaction of alcohols with phosgene, as described, for example, in Kirk-Othmer, Encyclopedia of Chemical Tecnology, 3a Ed., Vol.4, page 758.

As this procedure has various disadvantages, arising from the use of phosgene, alternative procedures have been devised of which the procedure based on the oxidative carbonylation of an alcohol, in the presence of suitable catalysts, has been particularly successful in the last few years.

The catalysts used in this oxidative carbonylation procedure are generally composed of copper compounds, as described for example in U.S. Patents 3.846.468, 4.218.391, 4.318.862, 4.360.477, 4.625.044, in published European Patent Applications 71.286, 217.651, and in the published German Patent Application 3.016.187.

The most widely-used method at present involves the use of a catalyst composed of cuprous chloride and is essentially based on the following reaction, examplified in the case of dimethylcarbonate.

$$2\ CH_3OH + CO + 1/2\ O_2 \rightarrow (CH_3O)_2CO + H_2O \qquad (I)$$

The procedure evolves through two phases of oxidation and reduction; without entering into the detailed mechanism of the reaction, it is presumed that in the first step the cuprous chloride reacts with methanol and oxygen to form a cupric methoxychloride which, in the second step, is reduced by the carbon monoxide with the production of dimethylcarbonate and the regeneration of cuprous chloride

$$2CuCl + 2CH_3OH + 1/2\ O_2 \rightarrow 2Cu(OCH_3)Cl + H_2O \qquad (II)$$

$$2\ Cu(OCH_3)Cl + CO \rightarrow (CH_3O)_2CO + 2CuCl \qquad (III)$$

This process however has a disadvantage due to the fact that the catalyst loses its activity over a period of time because of the loss of chlorine in the form of chlorinated products generated during the reaction.

EP-A-366177 discloses a process for preparing a di-alkyl carbonate via oxidative carbonylation of the corresponding lower alkanol (e.g. methanol, ethanol, propanol, isopropanol) in the presence of a catalyst system which comprises a copper alkoxy-halide and a quantity of between 0.5 and 10 mole % of HX with respect to the total moles of copper, where X is a halogen atom. This process also includes the separation of the reaction products from the catalyst by physical means (e.g. distillation, filtration etc.).

Published European Patent Applications 134.668 and 413.215 and EP-A-0460732 describe particular versions of the above procedure wherein the reaction products are continuously removed from the reaction mixture by evaporation induced by the saturation of the flow of gases fed into the reactor (CO, oxygen, possible inert gases).

Even in these processes, however, the problem of a decrease in the activity of the catalyst is not solved.

The Applicant has now found an improved process for the production of alkyl carbonates, and in particular dimethylcarbonate, starting from carbon monoxide, oxygen and alcohol, in the presence of a cuprous halide as catalyst, wherein the catalytic activity is stabilized by the addition of a halogenidric acid into the reaction system without causing any secondary reactions which would lower the yield of dialkylcarbonate.

This result is surprising in that it is well-known that the action of halogenidric acids on alcohols such as methanol or mixtures containing these alcohols, especially when the operating temperatures are higher than the room temperature, cause the formation of high quantities of alkyl halides and/or dialkylethers. In the case of methanol and hydrochloric acid these reactions may be summarized as such:

$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O \qquad (IV)$$

$$2CH_3OH \xrightarrow{HCl} CH_3OCH_3 + H_2O \qquad (V)$$

The present invention consequently relates to a process for the preparation of dialkylcarbonates with a high selectivity and a productivity generally higher than 20 and which can reach about 200 grams of dialkyl carbonate per litre of reactor volume per hour and which remains constant over an indefinite period of time, via oxidative carbonylation of the

corresponding lower alkanol in the presence of a cuprous halide catalyst, characterized in that the catalytic activity is stabilized by the addition of a halogenhydric acid into the reaction system, halogenhydric acid which is fed in such quantities as to maintain a ratio halogen/copper of about 1 in the catalyst.

According to one of the preferred methods of the procedures of the present invention the synthesis catalyst is composed of cuprous chloride and is preferably dispersed in methanol or ethanol.

During the synthesis of the dialkyl carbonate, which can be either a flow or batch process, the molar ratio between carbon monoxide and oxygen is usually higher than that of the stoichiometric value of the reaction and ranges from 3/1 to 100/1, preferably from 20/1 to 100/1, whereas the halogenidric acid, generally hydrochloric acid, is fed in such quantities as to maintain in the catalyst a ratio halogen/copper of about 1.

Quantities of acid of between 0.001 and 0.1 moles per mole of dialkyl carbonate produced, are normally used.

In practice the reaction is carried out by dispersing the catalytic system in the reaction medium, basically composed of alcohol possibly mixed with an inert solvent, such as a hydrocarbon, a halogenated hydrocarbon, an ester or ether, and putting this system in contact with the gaseous mixture of oxygen and CO.

The gaseous mixture which is put in contact with the alcohol dispersion, can be obtained either by pre-mixing the carbon monoxide and oxygen or alternatively by feeding the single gases separately and in this latter case contemporaneously or with alternating cycles.

It is also possible to use gaseous mixtures containing other gases, such as $H_2$, $N_2$, $CO_2$, $CH_4$, which behave as inert gases and do not cause secondary reactions in the reaction system. In particular it may be convenient, as described in U.S. Patent 4.318.862, to use carbon monoxide mixed with hydrogen.

The halogenidric acid may be added to the reaction system in a gaseous phase or as an aqueous or alcoholic solution. In the case of an aqueous solution, the concentration is preferably such as to limit the quantity of water introduced into the system, in that high concentrations of water diminish the selectivity and productivity of the reaction.

The halogenidric acid may be added directly into the synthesis reactor or pre-mixed with the reagents. It can be added either continuously or in batch, preferably continuously.

The reaction is conveniently carried out at temperatures ranging from 50 to 200°C, and, preferably, between 70 and 150°C, at a pressure ranging from the atmospheric value to 1013 MPa (100 atmospheres), preferably from 1,013 to 10,13 MPa (10 to 100 atmospheres) and with quantities of catalyst ranging from 10 to 300 g/l of liquid reaction mixture.

With respect to the recovery of the dialkyl carbonate, the conventional separating techniques may be used, such as distillation, filtration, decanting, centrifugation, demixing, absorption on solid absorbents or permeation through selective membranes. These recovery techniques may be used either alone or combined with each other.

The catalytic system and the non-converted reagents, together with any possible variable quantities of dialkyl carbonate and water, may be recycled to the carbonylation reaction.

In a specific version of the procedure of the present invention, in particular for the production of dimethylcarbonate, which follows the general lines already described in the above-mentioned EP-A-0460732, the separation of the reaction products is carried out in continuous by evaporation caused by the saturation of the flow of gases fed into the reactor. This solution has the advantage of avoiding, in a flow process, the movement and recycling of the catalyst to the synthesis reactor. The addition of hydrochloric acid into the system allows the stabilization, even at the highest possible productivity, of the catalytic system which would otherwise be rapidly deactivated.

In an example of this specific method, the procedure for the preparation in continuous of dimethyl carbonate includes:

a) feeding methanol, hydrochloric acid, carbon monoxide and oxygen into a reaction medium, kept under reaction conditions, basically containing a liquid mixture of methanol, dimethyl carbonate, water and a catalyst based on cuprous chloride;
b) removing a flow of vapours basically composed of methanol, water, dimethyl carbonate from the reaction mixture, said flow being present together with the gaseous flow basically containing carbon monoxide;
c) recovering the water and dimethyl carbonate from the vaporized mixture in a quantity substantially equal to that formed during the reaction and recycling the other components to the reaction environment;

the composition and volume of the liquid mixture, contained in the reaction environment, are substantially kept constant for a period of time, with a concentration of methanol equal to or higher than 30% by weight and with a concentration of water equal to or lower than 10% by weight of the mixture.

More specifically, the concentration of methanol in the reaction mixture may vary from 30 to 80% by weight and the concentration of water from 1 to 10% by weight. In the preferred method the process is carried out with a liquid reaction mixture having a composition within the following value ranges: methanol from 35 to 80% by weight and water from 2 to 7% by weight, the remaining percentage being basically composed of dimethyl carbonate and the inevitable impurities.

The following products are consequently fed in continuous to the above liquid reaction mixture: methanol, hydrochloric acid (possibly aqueous or methanolic), carbon monoxide, fresh and recycled, and oxygen possibly also together

with recycled dimethyl carbonate, the quantity of the fresh reagents being substantially equivalent to that converted in the reaction environment, or, with respect to hydrochloric acid, to the quantity of chlorine lost from the catalyst.

The following examples provide a better illustration of the present invention but do not limit it in any way.

EXAMPLE 1 (comparative)

3 litres of ethanol and 360 g of CuCl are charged into a internally enamelled reactor equipped with a reflux condenser.

The system pressurized with carbon monoxide at 2,45 MPa (25 kg/cm$^2$) is brought to a temperature of 135°C. A gaseous flow composed of 260 Nl/hr of carbon monoxide and 25 Nl/hr of $O_2$ are fed into the reactor. A flow of gases composed of non-converted carbon monoxide and oxygen and the $CO_2$ formed as a reaction by-product is released from the reactor, through the reflux condenser, operating under pressure control.

The reaction is interrupted after 4 hours.

After depressurizing the reactor, the liquid reaction mixture contained in the reactor is separated from the catalyst by evaporation under vacuum, collected and analysed.

3 litres of ethanol are freshly charged into the reactor, containing the catalyst used in the previous test, and the reaction is repeated as previously described.

10 reaction cycles are carried out in this way. The following table shows the % by weight of diethylcarbonate (DEC) obtained, in the reaction mixture collected after each single test:

| Test number | % DEC |
|---|---|
| 1 | 23.2 |
| 2 | 19.2 |
| 3 | 18.3 |
| 4 | 16.5 |
| 5 | 14.2 |
| 6 | 13.2 |
| 7 | 12.5 |
| 8 | 10.8 |
| 9 | 9.6 |
| 10 | 9.6 |

EXAMPLE 2

The procedure described in Example 1 is repeated also charging a 37% by weight aqueous solution of hydrochloric acid (HCl), as well as the ethanol, into the reactor at the beginning of the tests, starting from test no.7.

The quantity of acid added and the results obtained are shown in the following table:

| Test number | HCl 37%, $cm^3$ | % DEC |
|---|---|---|
| 1 | - | 22.2 |
| 2 | - | 20.4 |
| 3 | - | 19.1 |
| 4 | - | 16.3 |
| 5 | - | 14.2 |
| 6 | - | 13.3 |
| 7 | 60 | 14.8 |
| 8 | 12.5 | 19.4 |
| 9 | 12.5 | 19.3 |
| 10 | 12.5 | 19.1 |

EXAMPLE 3

The procedure described in Example 1 is repeated but using a 65% mixture of CO and $N_2$ in carbon monoxide instead of pure carbon monoxide and charging HCl into the reaction system in the quantities shown in the Table, which also indicates the results obtained.

| Test number | HCl 37%, $cm^3$ | % DEC |
|---|---|---|
| 1 | - | 14.6 |
| 2 | 15 | 11.1 |
| 3 | 15 | 12.9 |
| 4 | 15 | 13.7 |
| 5 | 15 | 13.3 |
| 6 | 15 | 11.4 |
| 7 | 15 | 12.6 |
| 8 | 15 | 10.4 |
| 9 | 15 | 11.4 |
| 10 | 15 | 13.0 |

EXAMPLE 4

Dimethyl carbonate is produced with a continuous process following the procedure described in EP-A-0460732.

A diagram of the apparatus used is shown in Figure (1) where the reactor R3 is an internally enamelled reactor, equipped with a stirrer and a thermal regulation jacket with diathermal oil, containing 10 l of reaction liquid and 2600 g of cuprous chloride catalyst (CuCl) equal to a concentration of 260 g/l. The reactor is pressurized to relative 2,35 MPa (24 kg/$cm^2$) and heated to 130°C.

The following products are fed into the reactor under normal conditions:

- 970 g/h (line 1) of fresh methanol;
- 8786 g/h (line 2) of a recycled liquid flow containing 77.3% by weight of methanol and 22.7% by weight of dimethylcarbonate;

- 15.7 g/h (line 3) of a 37% by weight aqueous solution of hydrochloric acid (5.8 g of 100% HCl);
- 1160 Nl/h (line 4) of a flow of carbon monoxide having a 93% purity in volume, the rest being composed of inert gases ($H_2$, $N_2$, $CH_4$, Ar);
- 235 Nl/h (line 5) of oxygen having a 98% purity in volume;
- 10500 Nl/h (line 6) of a recycled gaseous flow containing carbon monoxide 84% in volume, oxygen 0.7% in volume, carbon dioxide 4.5% in volume, the rest being mainly composed of inert gases.

The composition of the liquid mixture inside the reactor (R3) is the following: methanol 62.9%, dimethylcarbonate 32.2%, water 4.9% by weight.

The flow of gases and vapours leaving the reactor (R3), by line 7 is cooled in the exchanger CI at about 20°C and the liquid phase separated from the gaseous phase which goes through line 6, is recycled to the reactor R3 after cleaning with 860 Nl/h (line 8).

10.39 kg/h of a liquid mixture having the following composition are collected in V1: methanol 65.8% by weight, dimethylcarbonate 31.2% by weight, water 2.7% by weight and by-products 0.3% by weight.

1300 g/h of dimethylcarbonate (line 9) and 281 g/h of water (line 10) produced by the reaction are separated by fractionated distillation and demixing in S, whereas a flow of methanol and excess evaporated dimethylcarbonate is recycled through line 2.

From the previous data a 12.4% conversion of the methanol with a molar selectivity to dimethylcarbonate is determined calculated on 96% of methanol. The productivity is equal to 130 g of dimethylcarbonate per litre of solution and per hour.

The reaction is carried out in continuous over a period of 15 days without substantial variations in the standard conditions and productivity.

## Claims

1. Process for the preparation of dialkyl carbonates having high selectivity and productivity which remain constant over an indefinite period of time, via oxidative carbonylation of the corresponding lower alkanol in the presence of a cuprous halide catalyst, characterized in that the catalytic activity is stabilized by the addition of a halogenhydric acid into the reaction system, halogenhydric acid which is fed in such quantities as to maintain a ratio halogen/copper of about 1 in the catalyst.

2. Process according to Claim 1, wherein the synthesis catalyst is composed of cuprous chloride and is dispersed in methanol or ethanol.

3. Process according to Claims 1 or 2, wherein the molar ratio between carbon monoxide and oxygen is higher than the stoichiometric value of the reaction and is between 3/1 and 100/1.

4. Process according to any of the previous Claims, wherein the halogenidric acid is hydrochloric acid.

5. Process according to any of the previous Claims, wherein the halogenidric acid is fed in quantities ranging from 0.001 to 0.1 moles per mole of dialkyl carbonate produced.

6. Process according to any of the previous Claims, wherein the reaction is carried out at temperatures ranging from 50 to 200°C and at a pressure ranging from atmospheric pressure to 10,13 MPa (100 atmospheres), with quantities of catalyst ranging from 10 to 300 g/l of liquid reaction mixture.

7. Process according to any of the previous Claims, wherein the dialkyl carbonate is recovered by separation techniques such as distillation, filtration, decanting, centrifugation, demixing, absorption on solid absorbents or permeation through selective membranes.

8. Process according to claim 1, for the preparation in continuous of dimethyl carbonate by feeding into the reaction medium kept under reaction conditions, basically containing a liquid mixture of methanol, dimethyl carbonate, water and a catalyst based on cuprous chloride, a stream of methanol, carbon monoxide and oxygen, characterized in that together with this stream hydrochloric acid is also fed.

9. Process according to claim 8, characterised in that the concentration of methanol in the reaction mixture varies from 30 to 80% by weight and the concentration of water from 1 to 10% by weight.

## Patentansprüche

1. Verfahren zur Herstellung von Dialkylcarbonaten mit hoher Selektivität und Produktivität, welche über eine unbegrenzte Zeitdauer konstant bleiben, über eine oxidative Carbonylierung des entsprechenden niedrigeren Alkanols in Gegenwart eines Kupfer(I)-Halogenidkatalysators, dadurch gekennzeichnet, daß die katalytische Aktivität durch die Zugabe einer Halogenwasserstoffsäure in das Reaktionssystem stabilisiert wird, wobei die Halogenwasserstoffsäure in solchen Mengen zugeführt wird, daß ein Verhältnis von Halogen/Kupfer von ungefähr 1 in dem Katalysator aufrecht erhalten bleibt.

2. Verfahren nach Anspruch 1, worin der Synthesekatalysator aus Kupfer(I)-Chlorid zusammengesetzt ist und in Methanol oder Ethanol dispergiert ist.

3. Verfahren nach Anspruch 1 oder 2, worin das molare Verhältnis zwischen Kohlenmonoxyd und Sauerstoff höher ist als der stöchiometrische Wert der Reaktion und zwischen 3/1 und 100/1 liegt.

4. Verfahren nach einem der voranstehenden Ansprüche, worin die Halogenwasserstoffsäure Chlorwasserstoffsäure ist.

5. Verfahren nach einem der voranstehenden Ansprüche, worin der Halogenwasserstoffsäure in Mengen von 0,001 bis 0,1 mol pro mol hergestellten Dialkylcarbonats zugeführt wird.

6. Verfahren nach einem der voranstehenden Ansprüche, worin die Reaktion bei Temperaturen durchgeführt wird, welche von 50 bis 200°C reichen und bei einem Druck, welcher von Atomosphärendruck bis zu 10,13 MPa (100 Atmosphären) reicht, mit Mengen von Katalysator im Bereich von 10 bis 300 g/l der flüssigen Rekationsmischung.

7. Verfahren nach einem der voranstehenden Ansprüche, worin das Dialkylcarbonat durch Abtrennmethoden, wie z.B. Destillation, Filtration, Dekantieren, Zentrifugation, Entmischen, Adsorption auf festen Adsorbentien oder Permeation durch selektive Membranen gewonnen wird.

8. Verfahren nach Anspruch 1 zur kontinuierlichen Herstellung von Dimethylcarbonat durch Einspeisen eines Stroms von Methanol, Kohlenmonoxyd und Sauerstoff in ein unter Reaktionsbedingungen gehaltenes Reaktionsmedium, welches im wesentlichen eine flüssige Mischung aus Methanol, Dimethylcarbonat, Wasser und einen auf Kupfer(I)-Chlorid basierenden Katalysator enthält, dadurch gekennzeichnet, daß zusammen mit diesem Strom zusätzlich Chlorwasserstoffsäure eingespeist wird.

9. Verfahren nach Anspruch 8, dadurch gekennzeichnet, daß die Konzentration an Methanol in der Reaktionsmischung von 30 bis 80 Gew.-% variiert und die Konzentration von Wasser im Bereich von 1 bis 10 Gew.-%.

## Revendications

1. Procédé pour la préparation de carbonates de dialkyle ayant une forte sélectivité et productivité qui demeurent constantes pendant une période indéfinie, par carbonylation oxydative de l'alcanol inférieur correspondant en présence d'un catalyseur d'halogénure cuivreux, caractérisé en ce que l'activité catalytique est stabilisée par addition d'un acide halogénohydrique dans le système réactionnel, l'acide halogénohydrique qui est alimenté dans des quantités de façon à maintenir un rapport halogène/cuivre d'environ 1 dans le catalyseur.

2. Procédé selon la revendication 1, dans lequel le catalyseur de synthèse est composé de chlorure cuivreux et est dispersé dans le méthanol ou l'éthanol.

3. Procédé selon la revendication 1 ou 2, dans lequel le rapport molaire entre le monoxyde de carbone et l'oxygène est supérieur à la valeur stoechiométrique de la réaction et se situe entre 3/1 et 100/1.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'acide halogénohydrique est de l'acide chlorhydrique.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'acide halogénohydrique est alimenté dans les quantités allant de 0,001 à 0,1 mole par mole de carbonate de dialkyle produit.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel la réaction est conduite à des tem-

pératures allant de 50 à 200°C et à des pressions allant de la pression atmosphérique jusqu'à 10,13 MPa (100 atmosphères) avec des quantités de catalyseur allant de 10 à 300 g/l de mélange réactionnel liquide.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le carbonate de dialkyle est récupéré par des techniques de séparation telles que la distillation, la filtration, la décantation, la centrifugation, la ségrégation, l'absorption sur des absorbants solides ou la perméation à travers des membranes sélectives.

8. Procédé selon la revendication 1 pour la préparation en continu de carbonate de diméthyle par alimentation dans le milieu réactionnel maintenu dans des conditions de réaction, contenant en principe un mélange liquide de méthanol, de carbonate de diméthyle, d'eau et un catalyseur à base de chlorure cuivreux, un courant de méthanol, du monoxyde de carbone et de l'oxygène, caractérisé en ce que de l'acide chlorhydrique est également alimenté avec ce courant.

9. Procédé selon la revendication 8, caractérisé en ce que la concentration de méthanol dans le mélange réactionnel varie de 30 à 80 % en poids et la concentration d'eau de 1 à 10 % en poids.

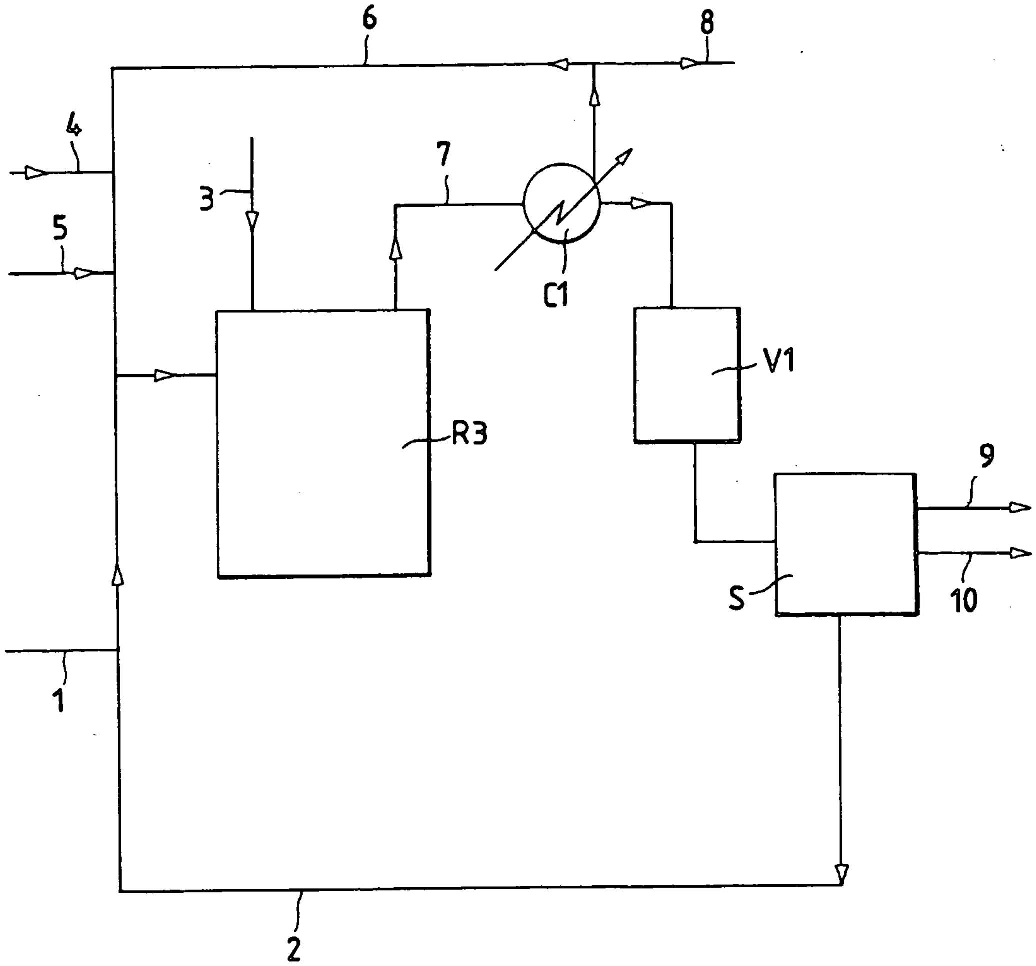


Fig. 1